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Development of cosmogenic 22Na as a tool to measure young water age in multiple watersheds

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A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelor of Science in Geology from
The College of William and Mary

by

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Abstract

Understanding residence time and flow rate of water is essential to monitoring and protection of water resources. Young fresh waters in particular are a vital resource that humans depend on today. Previous research has explored the viability of using cosmogenic sodium-22 (^{22}Na) to date young fresh waters. ^{22}Na is naturally produced in the atmosphere, scavenged by storms, and precipitated into water systems on the earth. ^{22}Na has a relatively short half-life (2.605 years), a currently stable atmospheric concentration, and conservative behavior in water, all of which are ideal for dating young water. An age for water can be derived by testing ^{22}Na in groundwater, stream water, and precipitation samples.

This study develops and tests three models for ^{22}Na-derived water age: the decay model, the ratio model, and the flux model. These models were tested in three different watersheds on the east coast of the United States: Hubbard Brook (Woodstock, New Hampshire), Jones Run (Shenandoah National Park, Virginia) and Pogonia Stream (Williamsburg, Virginia). Stream water collection methodology was significantly improved via an in-situ cation resin bag placed directly in the stream. The resin bag consistently collected samples that represented large volumes of stream water. Labor-intensive physical collection of stream water samples was thus unnecessary. This stream water resin was eluted with acid. Groundwater was analyzed for sodium concentrations. Precipitation and stream water was analyzed for sodium and ^{22}Na concentrations and fluxes.

Sodium concentrations in precipitation ranged from 0.02 mg/L to 0.14 mg/L. Stream water sodium concentrations ranged from 0.795 mg/L to 2.54 mg/L. When

analyzed for ^{22}Na, Hubbard Brook had a concentration of 0.162 mBq/L (± 0.01 mBq/L). Jones Run was found to have a ^{22}Na concentration of 0.063 mBq /L (± 0.007 mBq/L). Pogonia Stream had a ^{22}Na concentration of 0.04 mBq/L (± 0.01 mBq/L).

Stream water age, defined as the amount of time since the stream water was precipitation, was derived using the three ^{22}Na age models. The decay model provided problematic ages due to evapotranspiration artificially increasing concentrations of ^{22}Na. The ratio model age provided error due to sodium present in underlying stream geology, as well as sodium in throughfall rain. As the flux model is only affected by changes in ^{22}Na flux, it can be concluded the flux model provides the most accurate water age as compared to independently derived ages.

Introduction

People rely on clean fresh water for drinking, growing crops, and sustaining life; it is viewed as a precious dwindling resource. A complete analysis of water usage statistics indicates that the environmental problem of water scarcity is complex. Humans withdraw approximately 3,800 km^3 of water each year of the 45,500 km^3 total yearly discharge of fresh water on Earth (Oki and Kanae, 2006). If we are withdrawing less than 10% of the fresh water available to us, why is water scarcity a concern? The issue lies not with total fresh water volume, but rather its severely uneven spatial distribution. Clean water is an increasingly scarce resource in areas where it has been overexploited, and made all the more rare by contamination from urbanization and agriculture. A changing global climate causes some areas of the world to dry up while others are inundated by constant flooding. Approximately 3.1% of all deaths worldwide are caused by unsafe,

unclean, or inadequate water consumption (World Health Organization, 2002). These rapidly changing conditions require examination of our water resources. Young fresh waters in particular (defined as younger than 20 years old) are the most commonly used water supply and are extremely susceptible to anthropogenic contamination (Vörösmarty 2010). There is an urgent need to quantitatively track and asses the health of these most vital waters.

An important aspect of fresh water health is contaminant concentration and rate of movement. Scientists seek to understand how quickly a contaminant is moving through a given water system (transport rate) so they may understand how long it is expected to stay in the system (residence time). Being that the contaminant in a stream or groundwater system is carried along by the water, the rate of contaminant flow is determined by the rate of water flow. To quantify flows in streams and groundwater, scientists measure water age. Water age is defined as when ground or stream water was last precipitation; how long it has been in the earth's system. Plummer et al. (2003) define groundwater age as "the time elapsed since recharge—when the water entered the ground-water system." By measuring water age, we can begin to extrapolate the behavior of a soluble contaminant in that water.

Water age is typically measured using atmospheric tracers. An ideal tracer should precisely mimic the movement of the water with which it flows, with changes in concentration only due to defined processes (Strauch, 2014). Common atmospheric tracers used today are tritium (^3H), sodium hexafluoride (SF_6), and chlorofluorocarbons (CFCs). These few are known as "pulse tracers," as they were released into the atmosphere at once in large anthropogenic quantities. Current aging relies on comparing

the defined peak of anthropogenic concentration against current cosmogenic levels. As these anthropogenic concentrations change or decrease in the future, these methods will be rendered ineffective.

Trititum (^3H), sodium hexafluoride (SF_6), and chlorofluorocarbons (CFCs) have been used and tested for decades, although each has its own set of drawbacks. When tritium (^3H) dating was first developed for use in the early 1900's, water age was derived by comparing the water's concentration of ^3H to its natural atmospheric (cosmogenic) levels. In the period from 1953 to 1967, a high concentration of ^3H was released into the atmosphere during U.S. nuclear bomb testing (Egboka et al., 1983). Following this release, ^3H has been used for dating by comparing the water's concentration of ^3H with this well-defined anthropogenic peak (Figure 1). This huge peak has prevented cosmogenic ^3H from being used to date for the past 50 years, and will continue to render it useless for approximately another 40 years, until anthropogenic ^3H has decayed entirely (Fleishmann, 2008). As time passes, this large anthropogenic quantity is decaying and continually rained out, resulting in smaller and smaller amounts present in waters on Earth. When these increasingly smaller concentrations are used to date, they lead to a wider age range, giving ambiguous results (Plummer et al., 2003). Soon in the future, the anthropogenic concentration will reach zero, rendering this method useless.

Chlorofluorocarbons (CFCs) are also used as a tracer; they are present in the atmosphere purely from the manufacture and use of consumer products like refrigerators, air conditioners, and aerosol sprays (Jenkins & Smethie, 1996). CFCs used as tracers (such as CFC-11, CFC-12, and CFC-113) have no known cosmogenic source (Bauer et al., 2001). In dating water systems, scientists must account for interference from CFC

retardation, air mixing ratios, and adsorption to soils and sediments as water moves. These setbacks decrease the water's concentration of CFCs, resulting in a young age bias and a large margin of uncertainty to results. Since 1987, the banning of CFCs have led to a slow phasing out around the world; they are no longer being released in great quantities. The concentration of CFCs is slowly decreasing and will eventually lead to an atmospheric concentration of zero. The unpredictable behavior and decreasing concentration of CFCs will severely limits its future use as a tracer.

Sulfur hexafluoride (SF_6) is a very common water dating method, if used in preferential circumstances. It occurs naturally in the atmosphere in small amounts, but has a quickly accumulating anthropogenic concentration at a rate of 6% per year (Figure 1; Plummer et al., 2003). SF_6 does not experience retardation like CFCs, but its concentration can be similarly unpredictably changed. If water containing SF_6 is exposed to air, the gas will re-equilibrate with the current atmospheric concentration and lead to a young age bias. Mixed amounts of trapped air and SF_6 contamination from minerals and rocks (predominantly fluorite, with some granite contamination) also skews results (Busenberg and Plummer, 2000). SF_6's interference mechanisms and shorter travel time within water systems leads to an artificially younger age and age range – this also is not an ideal method.

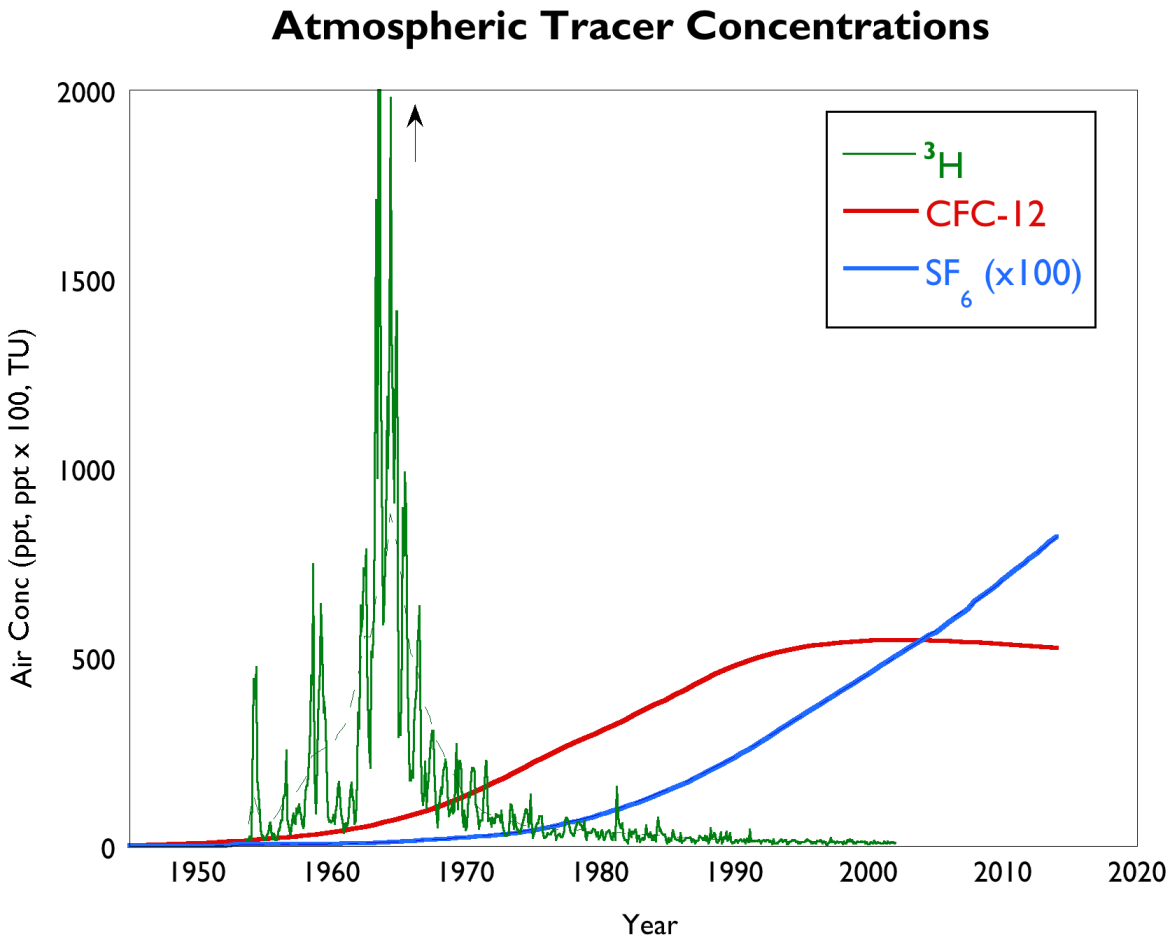

Figure 1. Common atmospheric tracer concentrations over time.

SF_6 and CFC age determination is performed by matching the tracer concentration in a water sample to a known atmospheric concentration. ^{3}H is a radioactive tracer and decays at a known rate. The age calculation is thus performed by incorporating its decay rate. The age of the water system can be predicted with a radioactive tracer using the standard decay equation (Equation 1):

$$N=N_0e^{-\lambda t} \quad (1)$$

Equation 1. Decay model.

In this equation, N is the concentration of the tracer at time t (mg/L), N_0 is the initial concentration of the tracer (i.e. in precipitation) (mg/L), and λ is the tracer decay rate ($time^{-1}$). Cosmogenic sodium-22 (^{22}Na) is a radioactive isotope of sodium, and a promising alternative for dating young waters (Fleishman 2008). A relatively short half-life (2.605 years), a currently stable atmospheric concentration, and conservative behavior in water makes ^{22}Na particularly suitable for dating young fresh waters. The concentration of ^{22}Na in water changes only due to decay and evapotranspiration.

The goal of this research is to further test the accuracy and develop the methodology of ^{22}Na as a tool to age young water. ^{22}Na has already been proven to provide accurate ages for a single stream's water and for a watershed on average against the established SF_6 method (Lauer, 2013 and Burton, 2014). To further this research, we must examine if the use of ^{22}Na is consistent in other similarly young watersheds. It is necessary to assess and cultivate the use of ^{22}Na as an isotopic tracer. As common methods begin to decline in efficacy, ^{22}Na will be the only sustainable tracer suitable for dating young waters.

Previous Work

The existence of ^{22}Na was discovered by Marquez in 1957, who noted its atmospheric origin and decay in rain water in Rio de Janiero, Brazil (Marquez, 1957). ^{22}Na occurs as a product of cosmic spallation from atmospheric Argon and secondary cosmic rays (Sakaguchi 2005; Figure 2a). It occurs in very low concentrations in the atmosphere, but is preferentially scavenged by and dissolves in precipitation, washing into the earth's water systems (Figure 2b). Anthropogenic ^{22}Na, like tritium, was released in 1950's and 60's nuclear testing, with a peak in 1966 (Cigna et al., 1970). The first attempts to use ^{22}Na for dating occurred in Russia in the 1970's, but were largely useless due to the still-present nuclear induced peak. However, ^{22}Na's short half-life (2.605 years) caused all anthropogenic concentrations to disappear by the 1980's. Today, we know specific production rates of ^{22}Na within the atmosphere and use the cosmogenic concentrations for measuring water age.

In studies examining ^{22}Na concentrations in water, trends in atmospheric production are observed. Measures of ^{22}Na concentrations in the air have found a dependence on four factors as defined by Leppänen et al.: (1) wet scavenging, (2) stratosphere-to-troposphere exchange, (3) vertical transfer in troposphere, and (4) horizontal transfer between different latitudes (2011). There also exist seasonal trends; the Lake Biwa study in particular found a maximum concentration in winter months and a minimum concentration in summer months (Sakaguchi, 2005).

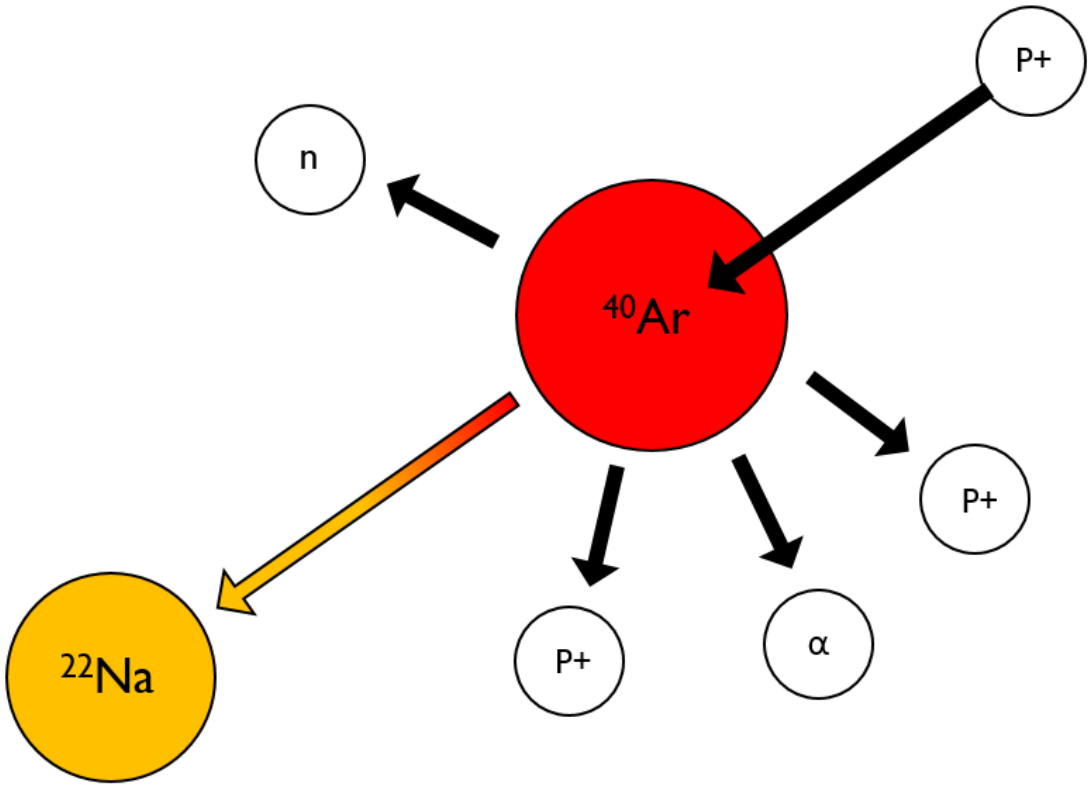

Figure 2a. A simplified diagram of creation of 22Na via cosmic ray spallation.

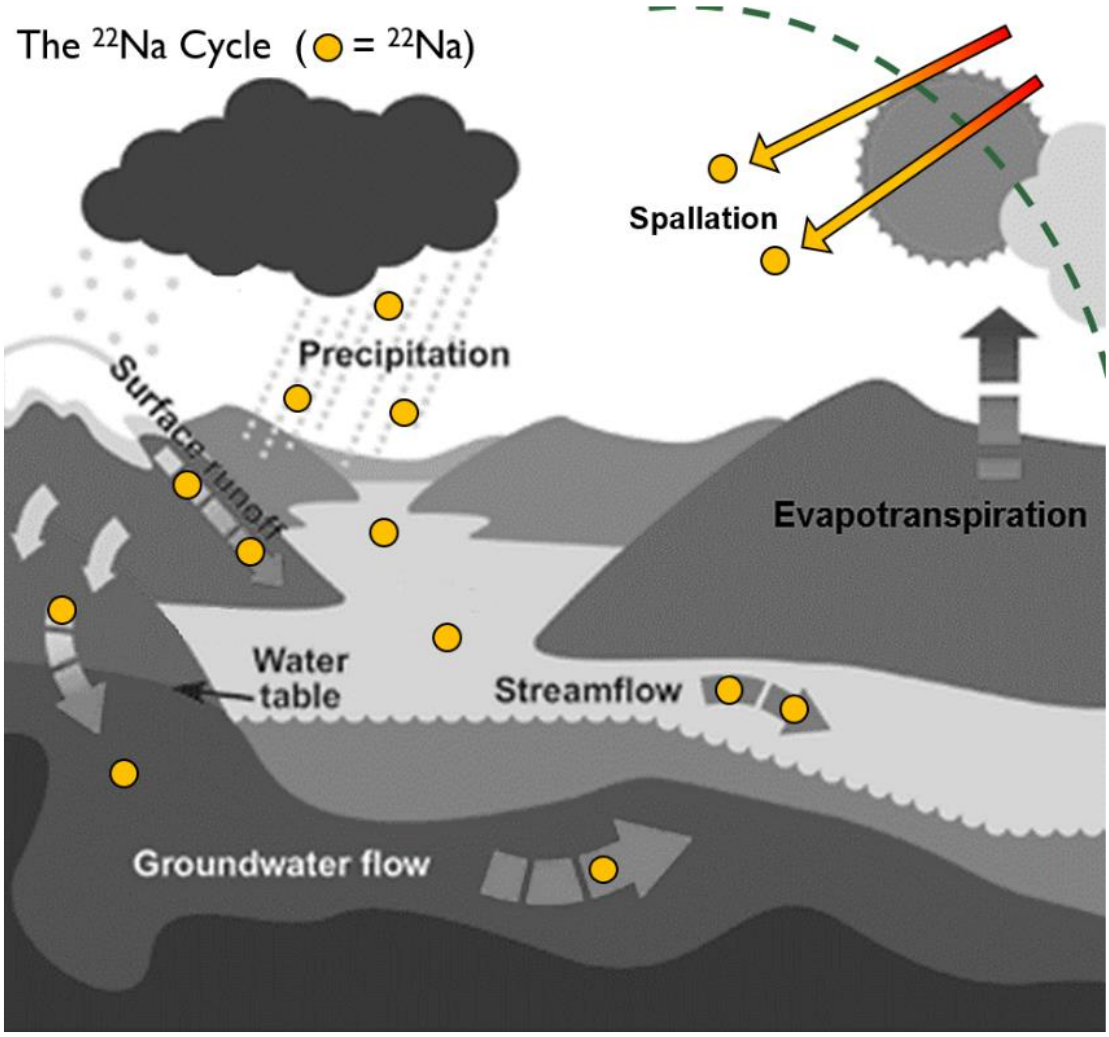

Figure 2b. A representation of the movement of 22Na throughout the hydrosphere. 22Na is created via spallation in the atmosphere. It is scavenged by storms, rained out onto the earth, and enters stream water and groundwater flow. Evapotranspiration does not contain 22Na (modified from Environment and Climate Change Canada).

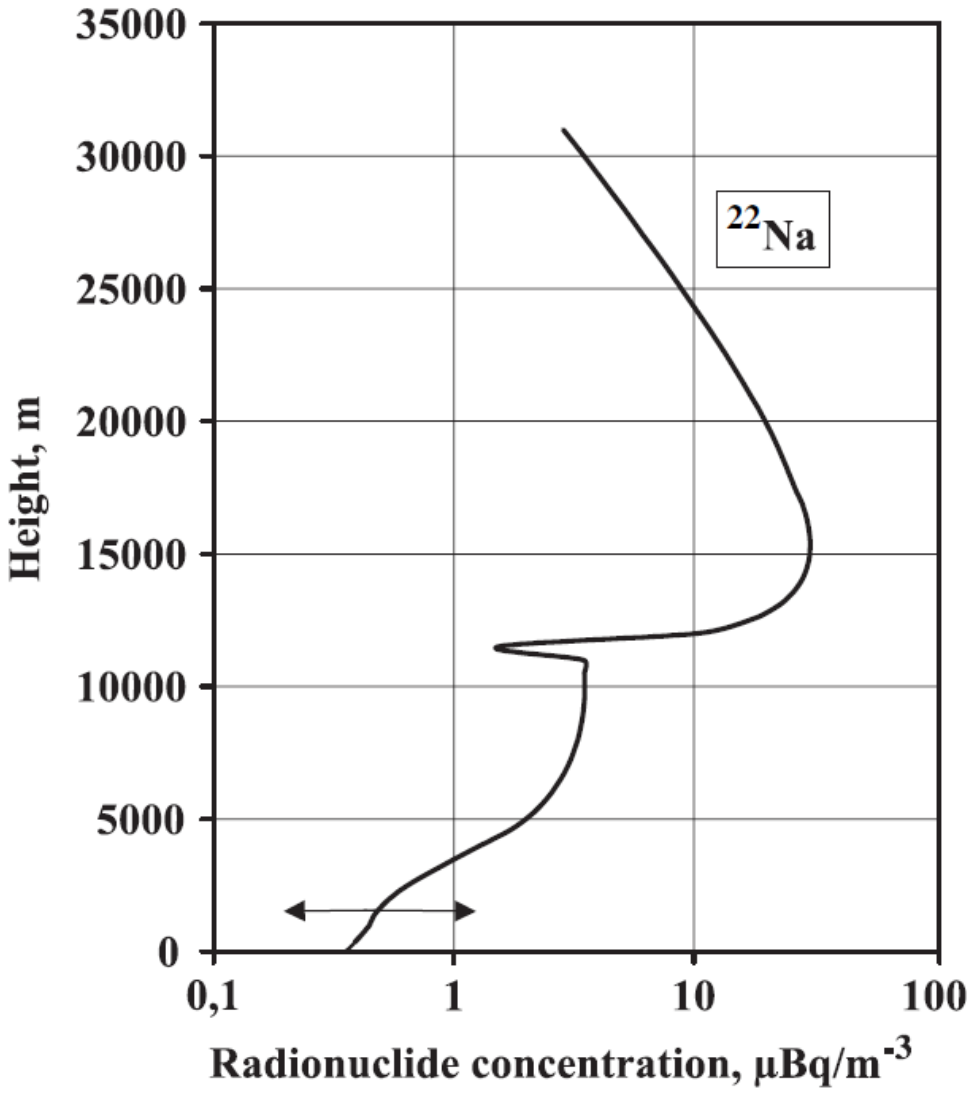

Figure 3. Distribution of the mean activity concentrations of ^{22}Na with altitude (modified from Jasiulionis, 2005).

To date, most research on ^{22}Na as a tracer has been performed in Europe and Asia. Recent research has been performed in the United States by previous students at the College of William & Mary. In Williamsburg, Virginia, research of ^{22}Na-derived water age has taken place from 2012 to the present. Nancy Lauer (2013) collected samples from February 2012 until January 2013. Alana Burton (2015) continued work until July 2014. Burton and Lauer quantified sodium concentrations and ^{22}Na concentrations and flux in precipitation and stream water.

The Williamsburg research site, the Pogonia Watershed, is located approximately two miles from the College of William & Mary campus and may be accessed from the Matoaka Trails off Strawberry Plains Road. The average ^{22}Na concentration measured at this site was ~100 $\mu Bq/m^3$ (Lauer 2013). Gamma spectroscopy analysis measured concentrations of ^{22}Na and provided an average age of 10 to 12 years for stream water of the Pogonia Watershed.

Lauer and Burton tested water age determination models in the Pogonia Watershed beyond the decay model (Equation 1). The concentration of ^{22}Na changes due to decay, but may also change due to evapotranspiration. Evapotranspiration can increase the concentration of ^{22}Na and provide a low age bias. This can be corrected for in a modified equation using a ratio model (Equation 2):

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$$\frac{[^{22}Na]}{[Na]} = \frac{[^{22}Na]_0}{[Na]_0} e^{-\lambda t} \quad (2)$$

Equation 2. Ratio model.

In this equation, [^{22}Na] is the concentration of ^{22}Na at time t (mBq/L), [Na] is the concentration of Na at time t (mg/L), [^{22}Na]$_0$ is the initial concentration of ^{22}Na (mBq/L), [Na]$_0$ is the initial concentration of Na (mg/L), and λ is the decay rate (time^{-1}). The ratio model is very similar to the decay model, albeit with the new element of [^{22}Na] divided by [Na]. Both ^{22}Na and Na behave conservatively in water, are biologically irrelevant, and are subject to change in concentration due to evapotranspiration. Only ^{22}Na changes due to decay. By dividing by [Na], we can correct for evapotranspiration.

The third model under consideration is the flux model. The flux model measures how much ^{22}Na is deposited onto a given area on an annual basis (Equation 3):

$$^{22}\text{Na stream flux} = (^{22}\text{Na precipitation flux})\, e^{-\lambda t} \quad (3)$$

Equation 3. Flux Model.

In this equation, ^{22}Na stream flux is the total annual flux of ^{22}Na exiting the watershed in stream flow (mBq/m^2), ^{22}Na precipitation flux is the total annual ^{22}Na flux into the watershed from precipitation (mBq/m^2), and λ is the decay rate (time^{-1}). Age calculation using ^{22}Na flux is not affected by evapotranspiration. Lauer argues the flux model is the best method for calculating stream water age. It may also be used to calculate ground water age by measuring aquifer discharge, but this is more difficult in practice in comparison to the decay and ratio models, where a discharge calculation is not necessary.

Methods

Precipitation + Groundwater Collection and Processing

Groundwater was collected from a series of wells in the Pogonia watershed. One section of 1 ¼ inch diameter screened PVC pipe was coupled to several 1 ¼ inch diameter solid PVC pipe sections to form a complete well. Holes for the wells were drilled using a manual auger until the water table was reached. One well was drilled using a truck mounted drill rig. The pipe was then inserted in the hole, and the space surrounding the well was filled with sand, backfill, and a bentonite clay cap. Three wells were self-installed in the Pogonia watershed. One previously installed well and a nearby pond were also sampled. These wells were installed at different points within the watershed with the intent of capturing groundwater at different flow points, to understand if age differences might exist within the watershed itself. Groundwater samples were brought back to the lab for measuring sodium concentrations on an ion chromatography machine.

Precipitation samples were collected monthly from February 2012 to July 2014 on the campus of the College of William & Mary, Williamsburg, Virginia. Monthly sampling continued in this study from February 2015 to February 2016. From a shed located behind McGlothin Street Hall, the shed roof rain gutters collected rainwater and snow melt from a total 40 ft^2 area. The runoff was then funneled through a coarse screen into a sealed rain barrel. At the end of each month, the rain barrel was completely emptied. 13 gallons of this water is collected in one-gallon jugs for ^{22}Na analysis. This large volume is needed to be able to remove a sufficiently large and testable amount of

^{22}Na. It is, however, smaller than previous collection requirements of 15-30 gallons, an improvement due to a greater efficiency in resin uptake and processing.

To process precipitation samples for ^{22}Na, 10-gallon Nalgene™ tanks are rinsed with a small portion of the collected water (1.5 gallons) to ensure removal of dust or remaining particles. The remaining 11.5 gallons of collected water is stored in the tank. A 6 ml aliquot is removed and analyzed using ion chromatography to test for total concentration of cations (Na, NH_4, K, Mg, Ca). From the IC-calculated concentration of each anion (mg/L), millimoles of charge/L and total millimoles of charge can be calculated. From this number, the total grams of cation resin to be added can be calculated. The calculated amount of wet cation resin (PCH) is added to the tank. Half as many grams of anion resin (PAO) is also added, to flocculate the cation resin. The water and resin is continually mixed via stir bar for 1 hour and 15 minutes to adsorb cations present in the water (Na as well as Ca, K, etc.). The stir bar is then turned off and the tank sits for 2 hours minimum to allow the resin to settle out and collect at the bottom of the tank.

At this stage, another 6 ml aliquot is removed from the tank to test effectiveness of cation removal via IC. Ideally, 90% or more of the cations have been uptaken. Focus remained on the uptake efficiency of sodium, the target cation. Once this has been achieved, the (resin-free) topmost nine-tenths of the tank water is decanted. The remaining (resin-containing) one-tenths of water is suction filtered through Whatman™ grade 40 filter paper (150 mm). The filter paper containing resin is placed in a crucible and oven dried at 100 °C for several hours, then weighed to record total pre-furnace

mass. The crucible is then put in a Thermolyne™ 1300 muffle furnace to burn at 600 °C for 24 hours, leaving only non-volatile cations after ignition.

1 ml of 1M strontium nitrate ($SrNO_3$) is added to the post-furnace crucible to elute the cations and bring them into solution. 10 ml of deionized water is added to bring up the volume of the sample. The resulting solution is placed on a hot plate at 135 °C to evaporate for 4 hours and 30 minutes. 30 µl aliquots are taken at 1 hour and 30 minute intervals to ensure full recovery of all sodium. The final sample, evaporated down to between 6 to 8 ml of liquid, is filtered to remove all solid particles. This resulting liquid is placed in a 12 ml quartz cuvette for final analysis.

Stream water: Field Sites

Stream water samples were collected from three sites on the east coast of the United States. Pogonia Stream (37°16'07"N, 76°44'19"W) has been sampled multiple times a year since 2012, and this study continues research at this site. A subset of the larger Matoaka watershed, the Pogonia Watershed is approximately 16 hectares in size. The watershed is predominantly forested, located behind a paved residential development. It is underlain by non-calcium or sodium containing Coastal Plain sediments. This prevents high calcium or sodium cation interference for an accurate age readings. The Pogonia watershed is an ideal setting for measuring ^{22}Na concentrations to determine a true water age.

Jones Run (38°13'40"N, 78°43'21"W) is located in Shenandoah National Park, in the Blue Ridge Mountains in northwest Virginia. Jones Run (and Shenandoah National Park at large) is a popular site for recreational hiking and fishing. Reclaimed from heavily

deforested land in 1935, Shenandoah National Park is now 95% forested by young trees (predominantly chestnut and oak forests). While Jones Run is open and accessible to the public, approximately 40% of Shenandoah National Park is federally designated as a protected wilderness areas. Jones Run can be accessed via hiking trails just under half a mile off of Skyline Drive. At 2690 feet in elevation, Jones Run is located in the South Fork sub-watershed within the larger James River Watershed. Jones Run itself is underlain by the western extent of exposed Catoctin greenstone in the Blue Ridge, and its watershed contains the Harpers and Weverton formations. The stream bed is sandy silt bedded with boulders.

Hubbard Brook (43°56'N, 71°45'W) is located in the Hubbard Brook Experimental Forest (HBEF), part of the White Mountain National Forest in New Hampshire. HBEF has served as an established research site since 1955, managed and protected by the USDA Forest Service. It includes within its boundary nine individual watersheds that have been studied for biological, hydrological, chemical, and geological purposes. The homogenous climate, vegetation, and geology of the area make it ideal for long term data collection. This study sampled a tributary of Hubbard Brook in Watershed 3. Watershed 3 is 42.4 hectares in size, ranging from 527 to 732 feet in elevation. It is underlain by quartz schist and quartzite bedrock of the Rangeley formation (Hubbard Brook Ecosystem Study).

Stream water Collection and Processing

Stream water was previously collected in the same manner as the precipitation samples; approximately 14 gallons was pumped directly from the stream into a tank for

processing. This study has since improved this methodology. To make field collection easier, the cation resin is sealed inside of a resin bag that is placed directly into the stream. 80-140 grams of Sigma Aldrich Dowex G-26 H-form cation resin is placed into a screened bag approximately 3x8 inches in size. The resin beads have a diameter constraint of 600-700 micrometers; using 250 micrometer screen material ensures none of the resin will be lost to stream flow. This bag is laid at the bottom of the stream and aligned with the flow direction. The resin can thus freely mix with the water, and cations can more easily sorb to the resin (Figure 4). After 3 to 4 days minimum, the resin bag is retrieved from the stream and brought back to the lab. 60 ml stream water samples are taken at the beginning and the end of the 3 to 4 day period to analyze for total sodium concentration in the stream.

To process the stream water, the resin is placed in a chromatography column. To remove the sodium from the resin, elution is performed with 1M hydrochloric acid. The acid is dripped onto the resin using a peristaltic pump at a rate of 1 ml/minute. The resulting drip-through is collected in 50 ml intervals. From each 50 ml interval, diluted 30 µl aliquots are analyzed on the IC machine for cation concentration. Ideally, 90%+ of the total sodium is eluted in the first 300 ml (Figure 5). Once total elution of the sodium is complete, the sodium-containing liquid is evaporated down to a volume of 6 to 8 ml. This resulting liquid is placed in a 12 ml quartz cuvette for final analysis.

Figure 4. A picture of a resin bag placed in Pogonia Stream (outlined in red). Water flow direction is indicated by the blue arrow. Placing the resin bag lengthwise in the stream ensures maximum contact with stream flow and exchange of cations with the resin. The circles visible in the bag are weights.

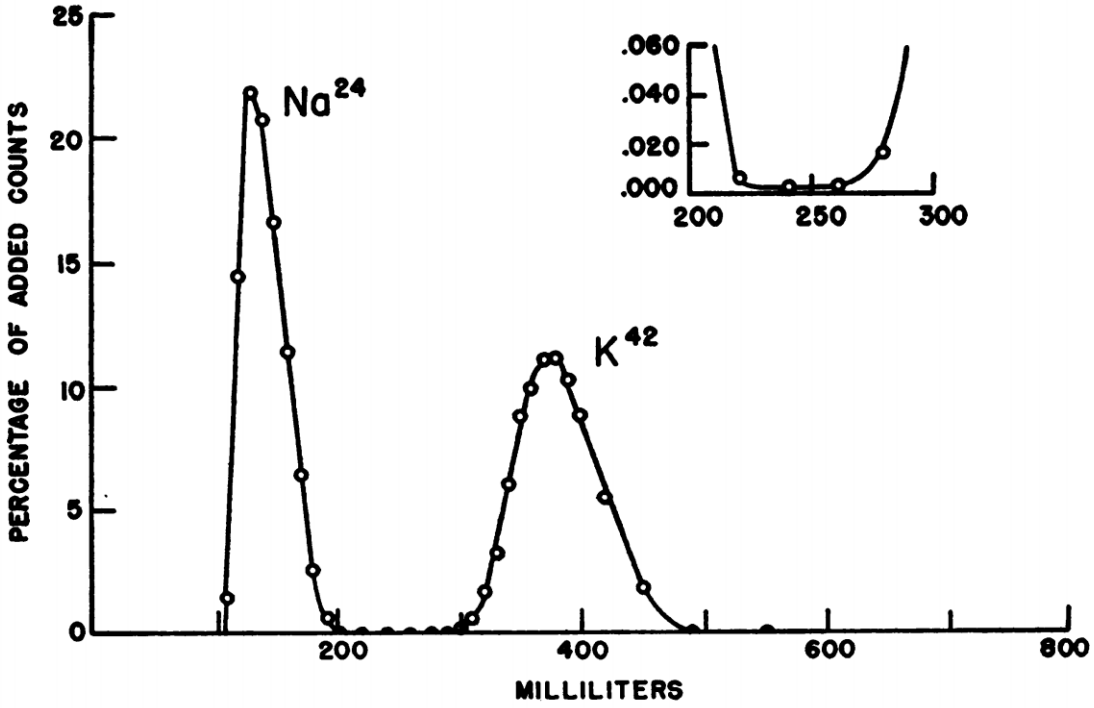

Figure 5. Ideal removal of cations with milliliters of acid eluent. The goal is to remove as much sodium as possible without crossing over into eluting much potassium. The above is results from a test the authors performed with similar parameters to this research: Dowex 50 resin, 8 x 1.3 cm column, flow rate of 0.74 ml/min, at room temperature (Arons & Solomon, 1954).

Sample Analysis

To determine water age, the ultimate goal for any water sample is to quantify the amount of ^{22}Na present. To do this, measurement of ^{22}Na is performed through its decay emissions. An atom of ^{22}Na decays to ^{22}Ne every few seconds and can happen through one of two mechanisms: electron capture or positron decay (Figure 6). Typically, a low background Intrinsic Germanium Detector (located in Millington Hall on the College of William & Mary campus) is used to count the electron capture gamma emission at 1274.5 keV.

A new method of gamma spectroscopy was tested on samples. Sodium iodide (NaI), bismuth germinate oxide (BGO), and photomultiplier tube (PMT) detectors measured gamma emissions at 1274.5 keV from both electron capture and positron decay. (Figure 7) Another component of positron decay involves positron (β+) electron annihilation, releasing two perpendicular gamma rays at 511 keV. To develop detection efficiency, these 511 keV emissions were measured using a coincidence detection method. Scintillation cocktail was added to the cuvette containing the sample. The sample, placed between two detectors facing each other, emitted a flash of light when the positron emission hit the scintillation cocktail. The photomultiplier picks up a flash of light every time a positron is emitted, while the BGO and NaI detectors picks up the physical 511 keV gamma emission. Counting any emission hits from a sample produced a gamma spectrum, where ^{22}Na can be limited to those gammas being produced at 511 keV or 1274.5 keV. By limiting hit counts to the coincidence of perpendicular 511 keV emissions (which occur almost simultaneously), one can significantly decrease background noise and be sure any hit is due to the presence of ^{22}Na.

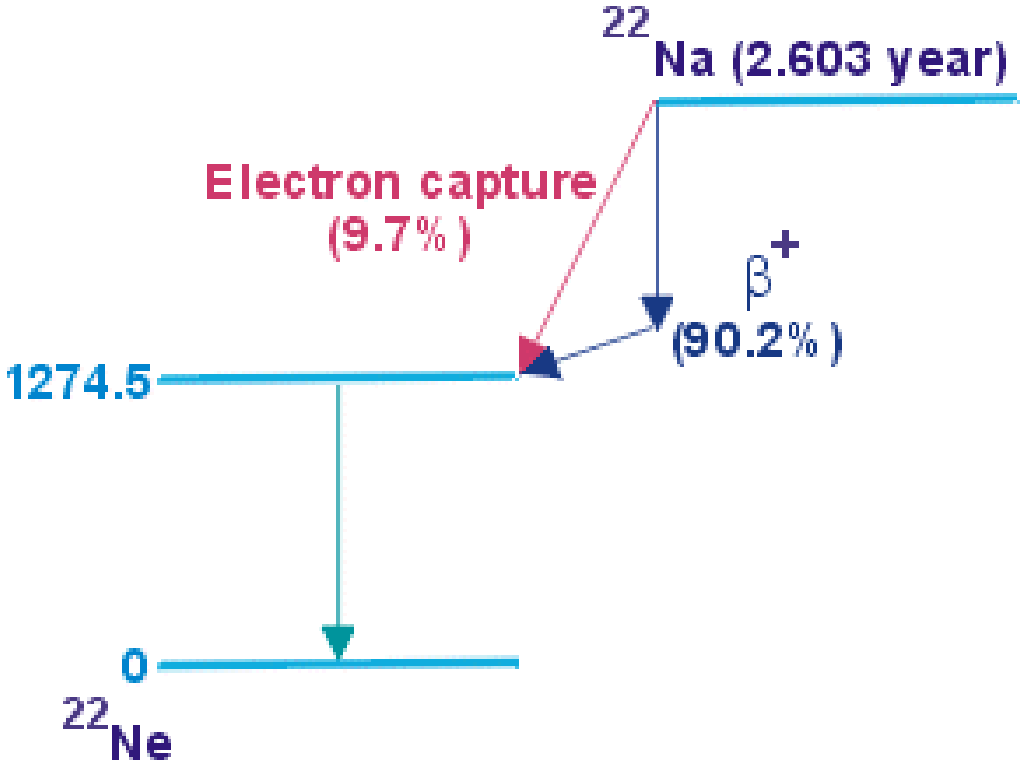

Figure 6. 22Na decay scheme. (modified from University of Liverpool Physics)

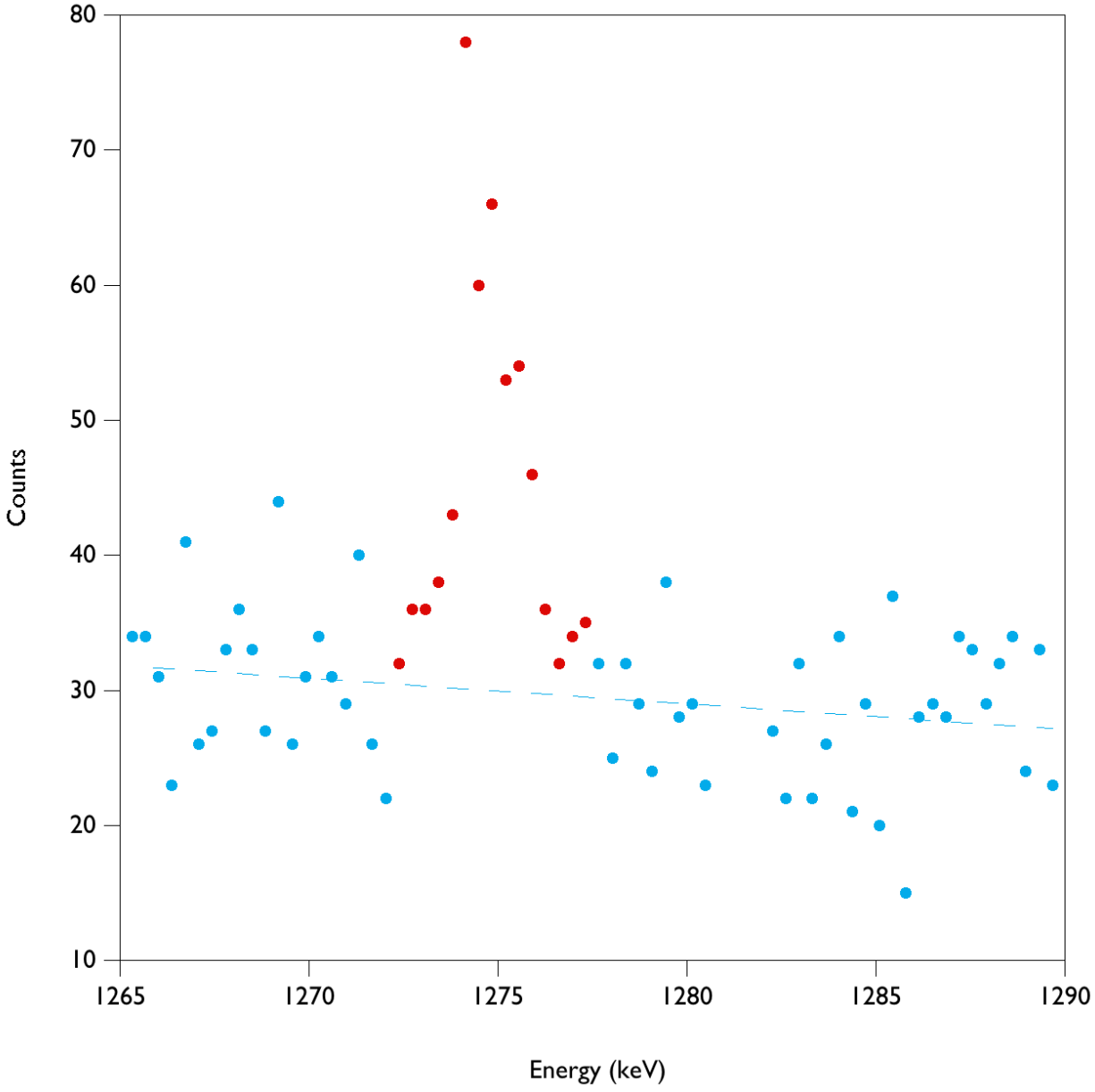

Figure 7. A gamma spectrum from the Hubbard Brook sample showing a distinct 22Na peak at 1274.5 keV.

Age Determination

In calculating total age for the watersheds, all three aforementioned models were examined (decay model, ratio model, and flux model). All three models are reproduced below:

$$N=N_0e^{-\lambda t} \quad (1)$$

Equation 1. Decay model.

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$$\frac{[^{22}Na]}{[Na]} = \frac{[^{22}Na]_0}{[Na]_0} e^{-\lambda t} \quad (2)$$

Equation 2. Ratio model.

$$^{22}Na \text{ stream flux} = {}^{22}Na \text{ precipitation flux} \bullet e^{-\lambda t} \quad (3)$$

Equation 3. Flux Model.

The flux model requires a calculation of discharge to calculate the ^{22}Na stream flux. This information is not readily available for any and all potential sites. To calculate discharge, the percent evapotranspiration model is used, derived from Sanford and Selnick (2013):

$$Q = \%\ ET \bullet P \quad (4)$$

Equation 4. Percent Evapotranspiration model.

In this equation, Q is the annual discharge of the river (L/m^2), % ET is the percent of precipitation lost to evapotranspiration, and P is the annual precipitation (L/m^2). The authors created a regression equation for streamflow and precipitation based on land cover and climate data from 838 watershed across the United States from 1971-2000. They propose a simple water balance equation where the volume of precipitation in a given area is equal to the volume of water lost to evapotranspiration plus the volume of

stream discharge. By using annual discharge averaged over a long 30 year period, changes in groundwater volume storage were assumed negligible compared to stream discharge. For a comparable result in this study, 13-30 years of annual rainfall data was used for each site.

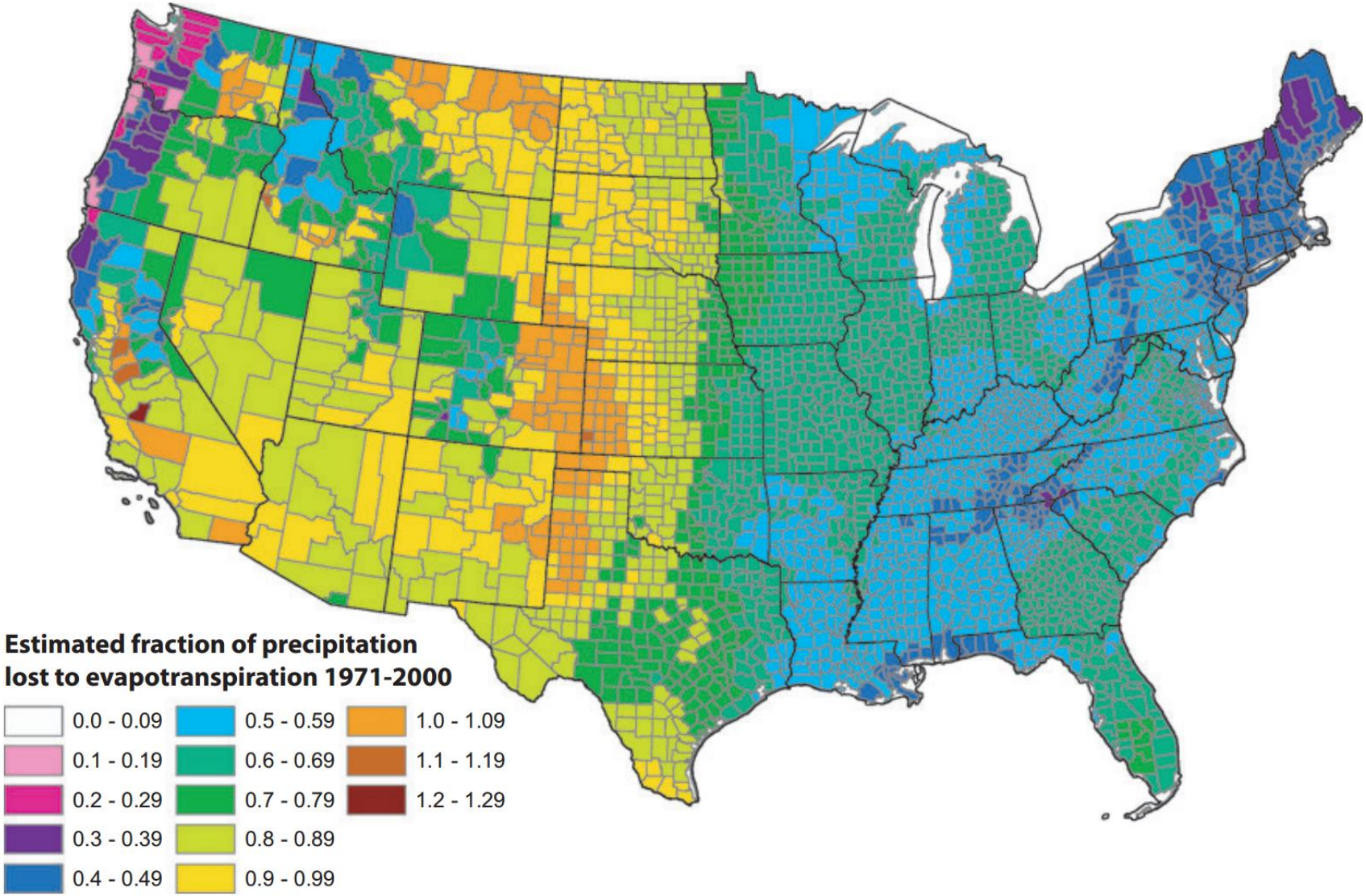

Figure 8. Percent Evapotranspiration. Percent of precipitation lost to evapotranspiration. In the three study areas, % ET ranges from 0.4-0.59. (Sanford and Selnick, 2013)

Results

Determination of Na and ^{22}Na Levels

Sodium concentrations were measured in all four groundwater wells, along with an uphill pond and Pogonia Stream itself. Among all sampled sites, sodium concentrations were very similar, ranging from 2.57 mg/L to 3.51 mg/L (Table 1). The one outlier, the Hillslope Well, had an average concentration of 9.54 mg/L of sodium.

Site	Abbreviation	Average [Na] (mg/L)
Valley Well	VW	2.97
Alana Well	AW	2.59
Hillslope Well	HW	9.54
Bailey Well	BW	3.51
Pond	Pond	3.02
Pogonia Stream	Pag	2.57

Table 1. Sodium concentration in wells in the Pogonia Watershed.

Calibration samples and precipitation samples were tested in development of NaI, BGO, and PMT detection. Testing of sample-to-cocktail ratios proved 1M 40% by volume samples (40% sample, 60% scintillation cocktail) yielded the clearest and most consistent samples. Analysis of the May 2015 precipitation sample provided a ^{22}Na flux of 8.55 mBq/m^2. The June 2015 precipitation sample was found to have a ^{22}Na flux of 9.67 mBq/m^2. Further data and preliminary results can be found in Appendix A.

Determination of sodium levels in precipitation was made through periodic collection from single storms. In analyzing precipitation collection methodology, comparison of throughfall and rainfall concentrations of sodium (mg/L) were made. Sodium concentrations were on average 3.28 times greater in throughfall than in rainfall.

Sodium concentrations in open rainfall ranged from 0.025 mg/L to 0.565 mg/L. In throughfall, sodium concentrations ranged from 0.073 mg/L to 1.160 mg/L (Figure 9a).

Calculations of flux (determined from the 1m x 1m collection bins) found a similar trend. Sodium flux (mg/m^2) on average was 2.61 times greater in throughfall than in open rainfall. Flux in open rainfall ranged from 0.093 mg/m^2 to 1.693 mg/m^2. In throughfall, flux ranged from 0.241 mg/m^2 to 6.38 mg/m^2 (Figure 9b; Appendix B).

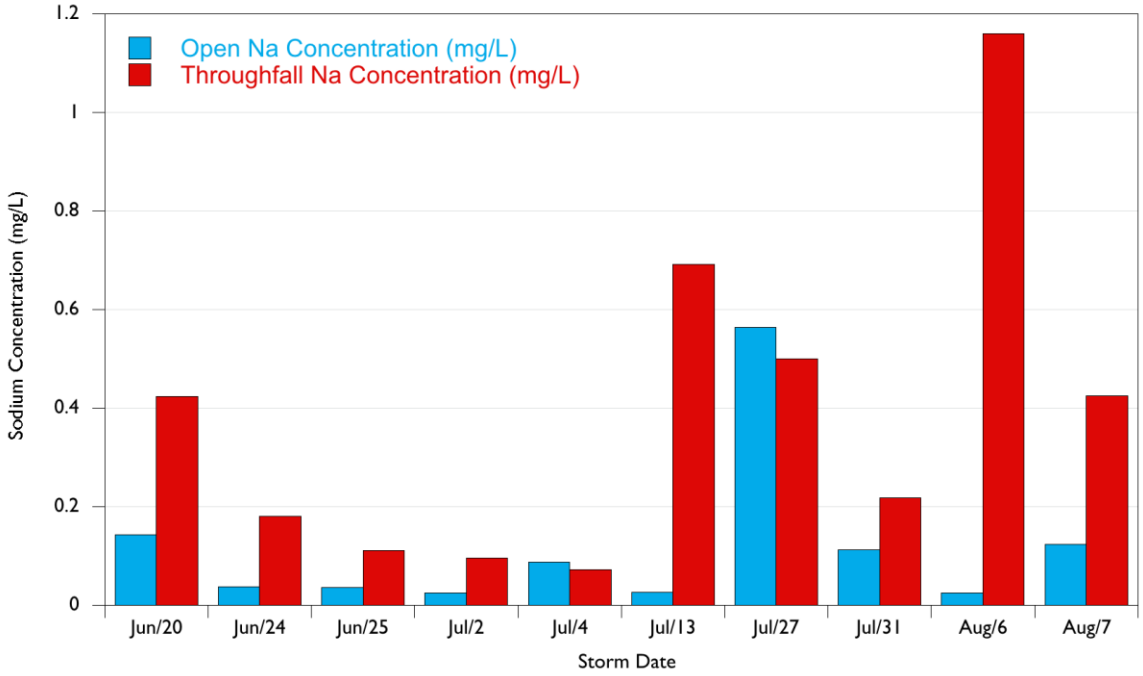

Figure 9a. OvT Sodium Concentrations. A graph showing the average sodium concentration in mg/L for a single rain event in open rainfall collectors vs. throughfall collectors.

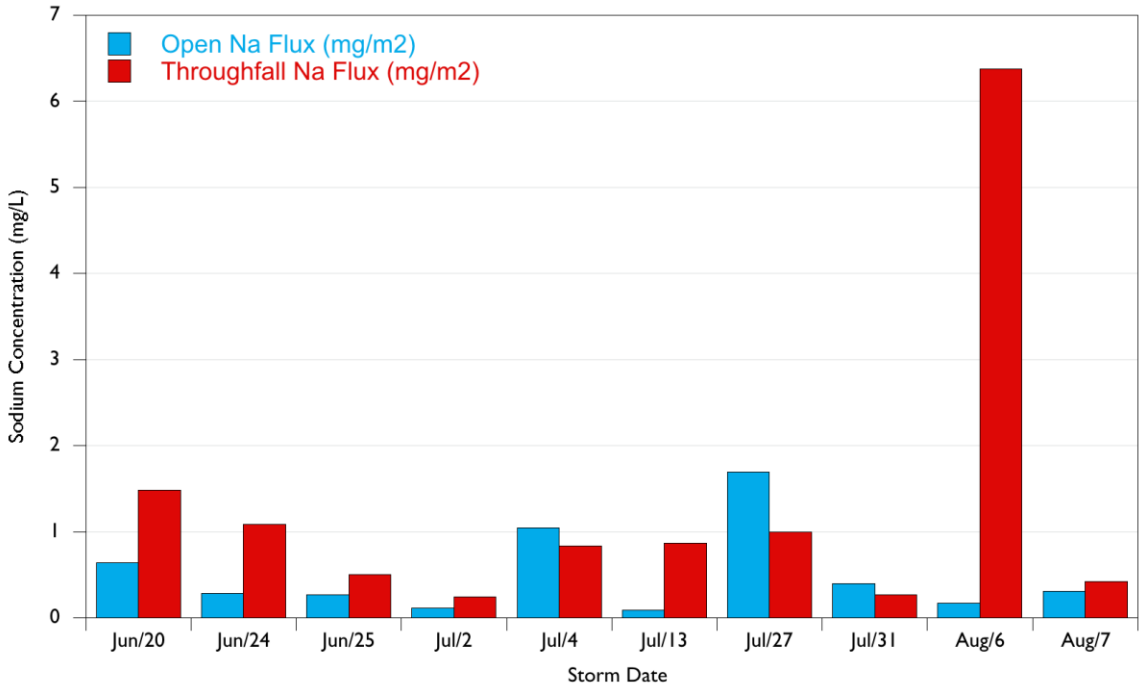

Figure 9b. OvT Sodium Flux. A graph showing the average sodium flux in mg/m^2 for a single rain event in open rainfall collectors vs. throughfall collectors.

^{22}Na Resin Collection Development

Resin efficiency for precipitation and groundwater cation and anion resin improved from previous research. For a 90%+ uptake of sodium cations, previous research required 2.632 and 3.704 grams of resin per mmol of charge; the current method requires 2.273 grams (Table 2).

Research	Resin required for 90%+ cation uptake (g)
Lauer (2013	3.704
Burton (2015)	2.632
Goydan (2016	2.273

Table 2. Resin needed for 90%+ uptake. A table showing increased resin efficiency over time.

Elution of stream water collection resin yielded sodium peaks between 0-300 ml. Total elution was refined and performed up to 550 ml in later samples. Hubbard Brook resin elution yielded a total mass of 307.56 mg of sodium. Jones Run resin elution yielded a total mass of 96.78 mg of sodium. The first Pogonia resin elution yielded a total mass of 120.80 mg of sodium. The second Pogonia resin elution yielded a total mass of 88.95 mg of sodium. (The two Pogonia samples were combined for analysis, for a total of 209.75 mg.)

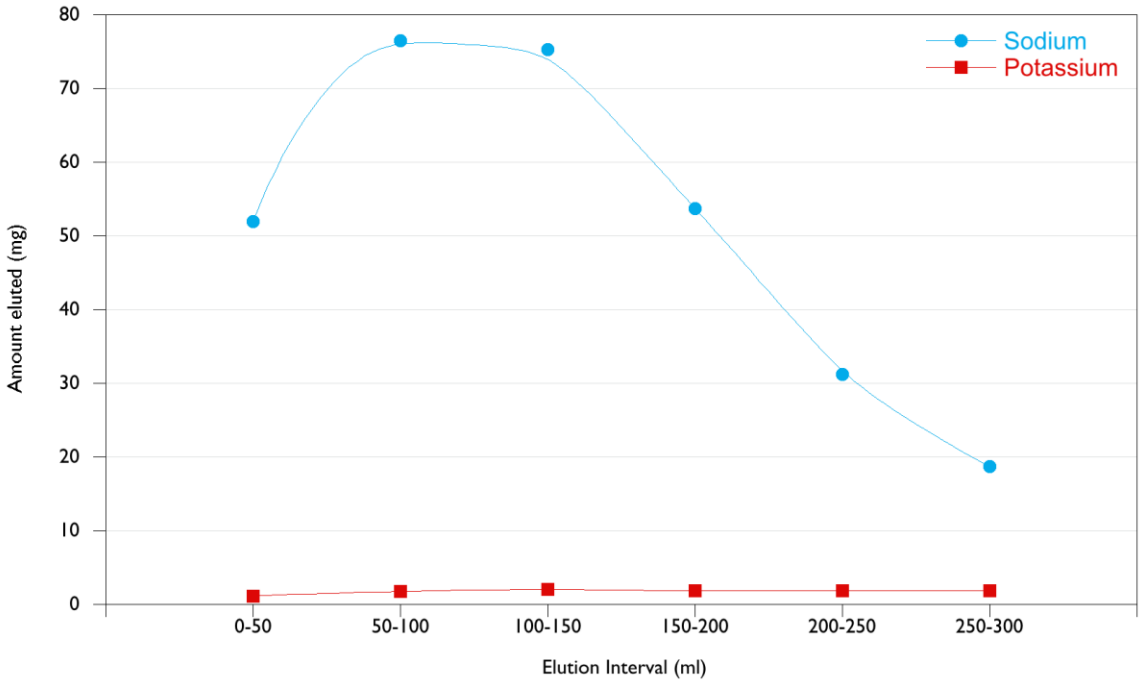

Figure 10. Hubbard Brook Resin Elution. A plot showing the amount of sodium and potassium eluted in each acid elution interval.

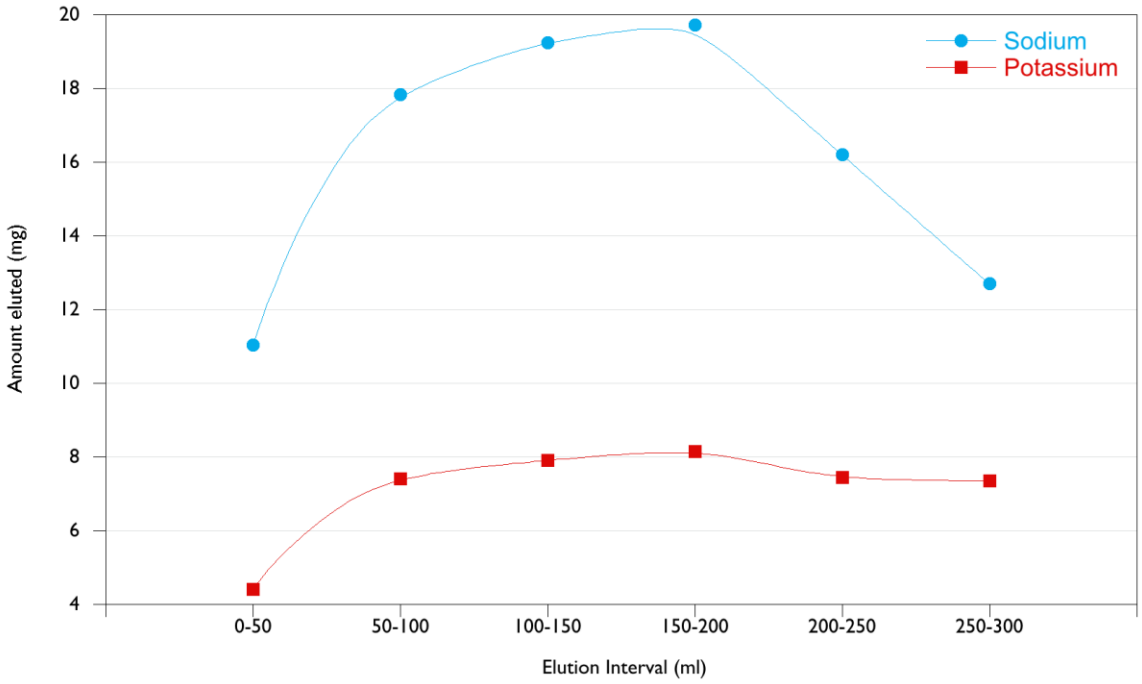

Figure 11. Jones Run Resin Elution. A plot showing the amount of sodium and potassium eluted in each acid elution interval.

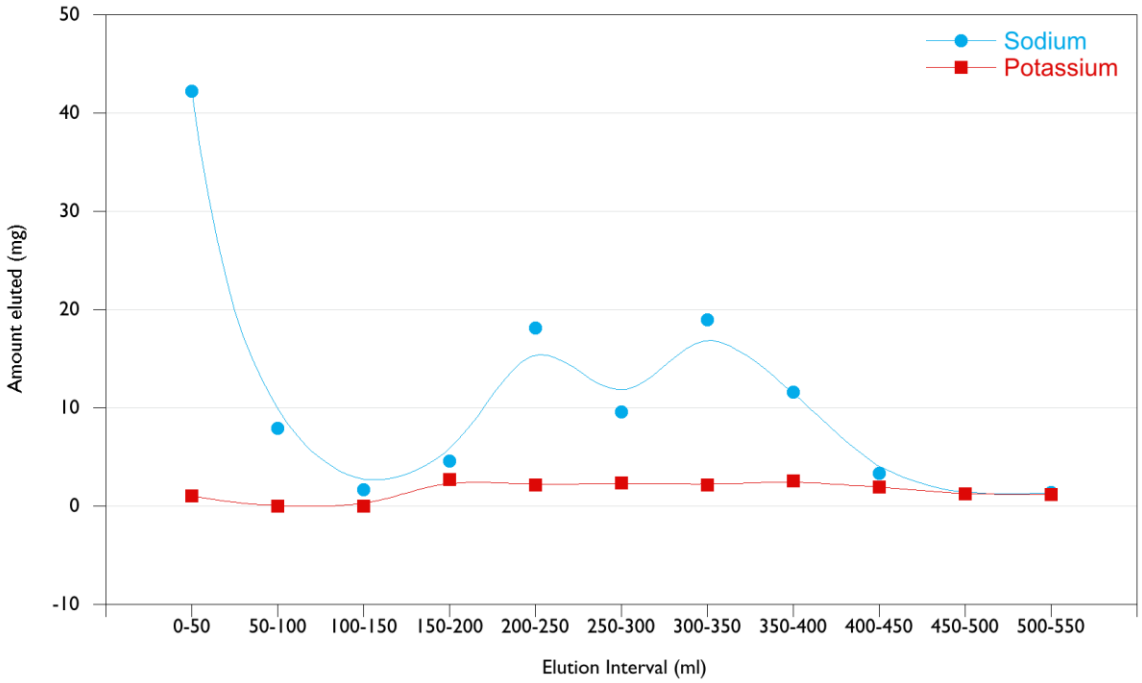

Figure 12. Pogonia Stream I Resin Elution. A plot showing the amount of sodium and potassium eluted in each acid elution interval.

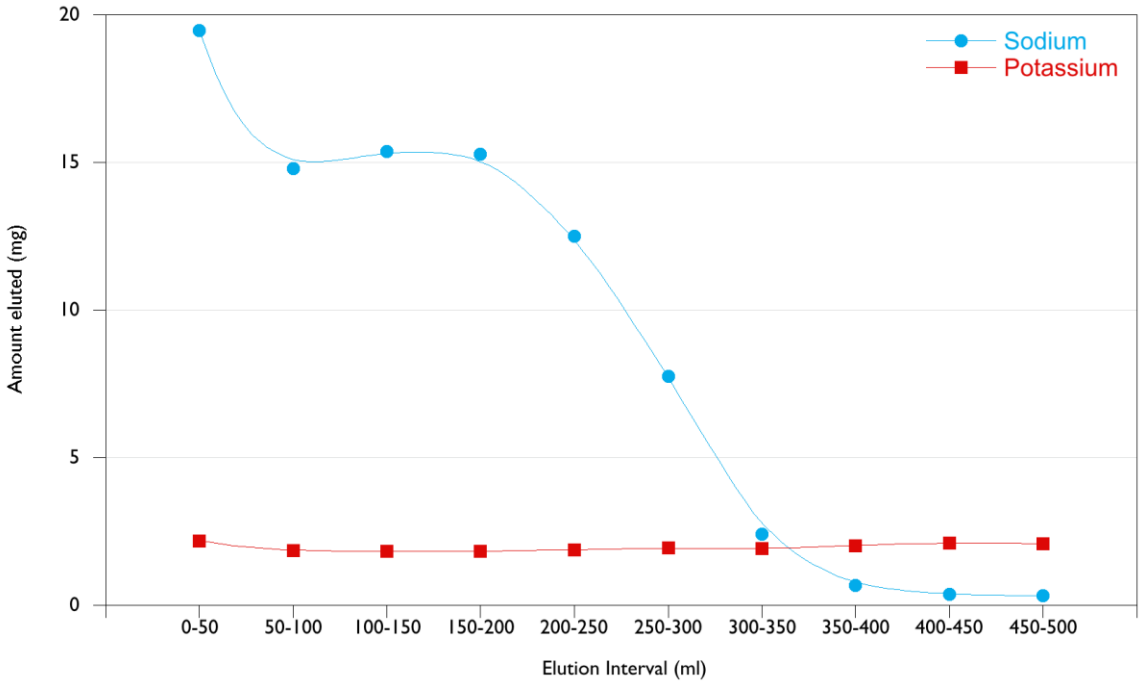

Figure 13. Pogonia Stream II Resin Elution. A plot showing the amount of sodium and potassium eluted in each acid elution interval.

The equivalents liters collected via the resin bag stream water collection method could be calculated by dividing the total sodium collected by the resin (mg) by the ambient stream sodium concentration (mg/L) (Appendix C). For a significant level of ^{22}Na to be measured in stream water samples, a general rule of thumb for collection is a minimum of 80 liters (Burton 2015). The resin bag consistently equilibrated with a volume of water equivalent to previous water collection methods (Table 3; Appendix C).

Sample	Liters Equilibrated
Hubbard Brook (8/29/15-9/1/15)	169
Jones Run (9/19/15-9/25/15)	122
Pogonia Stream I (10/19/15-10/22/15)	51
Pogonia Stream II (2/11/16-2/15/16)	35

Table 3. Total liters equilibrated in each resin bag collection period.

The samples were analyzed for ^{22}Na concentrations from the eluted solution. Hubbard Brook had a concentration of 0.162 mBq/L (± 0.01 mBq/L). Jones Run was found to have a ^{22}Na concentration of 0.063 mBq /L (± 0.007 mBq/L). Pogonia Stream had a ^{22}Na concentration of 0.04 mBq/L (± 0.01 mBq/L).

Discussion

Determination of Na and ^{22}Na Levels

Groundwater sodium concentrations were examined to find groundwater flow paths within the Pogonia Watershed. If groundwater flow paths could be determined, water age could be calculated at discrete points within the watershed, with the youngest water found at the watershed ridge, and the oldest water found closest to the stream. In line with this theory, sodium concentrations in groundwater would be expected to be smallest at the watershed ridge, and greatest closest to the stream as evapotranspiration occurs while the groundwater travels.

Measurement of sodium concentration in groundwater wells found relatively consistent concentrations among all wells, from 2.57 mg/L to 3.51 mg/L. There was no trend found with regard to elevation or distance to stream at all sampling sites (Figure 14). The similarity of sodium concentrations implies that rather than discrete flow paths occurring underground in the Pogonia Watershed, there was more likely a mixing of all present groundwater. At the small scale of the Pogonia Watershed, groundwater flow paths cannot be isolated and the age of groundwater as it moves on the hillslope cannot be determined. The one outlier, the Hillslope Well, had a higher concentration of sodium at 9.54 mg/L. This may be due to a perched water table or a lens of pre-existing sea water trapped in the underlying Coastal Plain sediments.

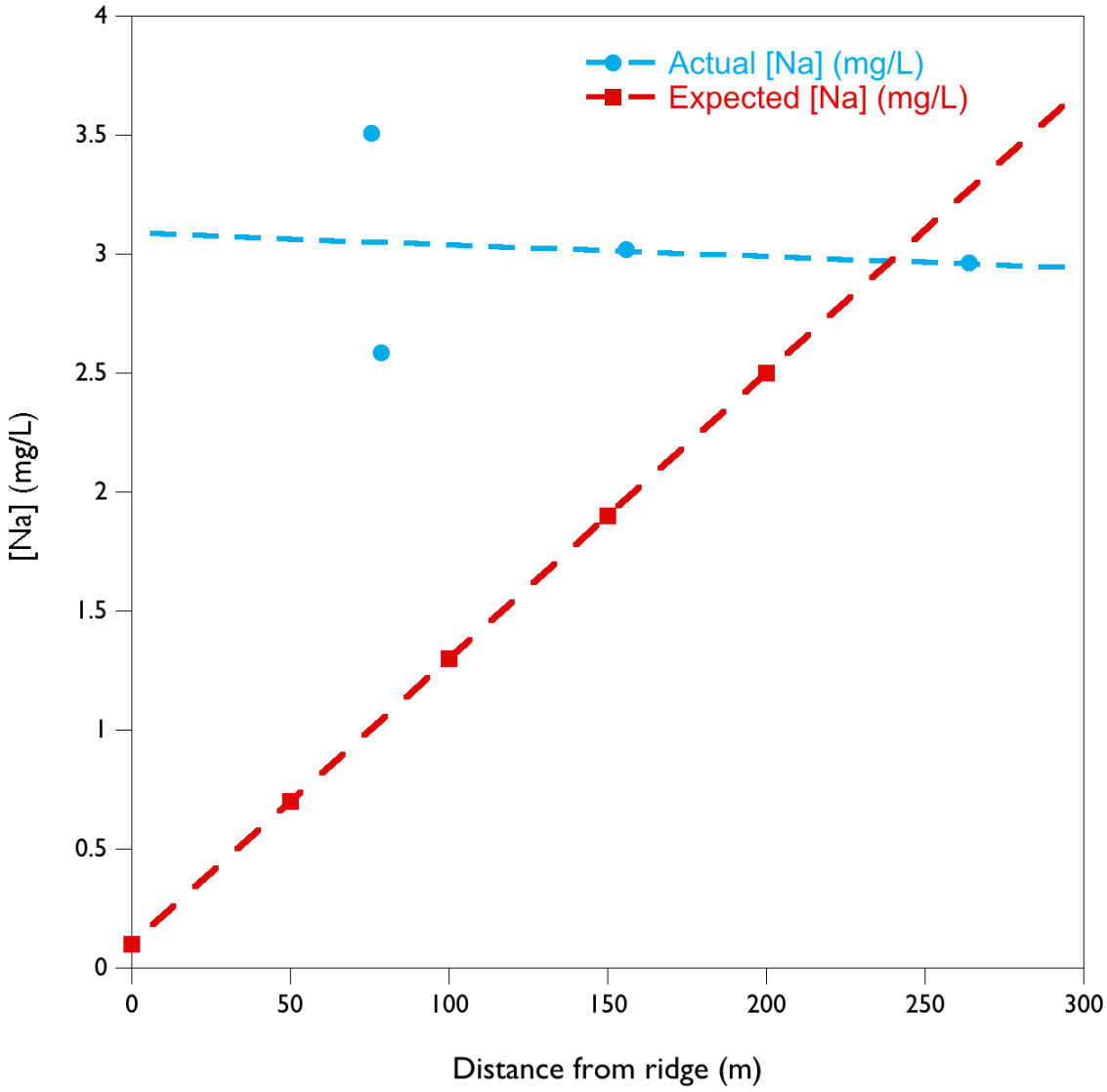

Figure 14. Pogonia Watershed sodium concentrations with distance from watershed ridge.

For ^{22}Na model testing, ^{22}Na levels had to be determined in precipitation and stream water for all three sites. For the decay and ratio models, ^{22}Na concentrations in stream water were directly measured via resin bag collection. ^{22}Na concentration in precipitation was found to be 0.13 mBq/L, as determined from a volume weighted average of ^{22}Na concentrations in precipitation in Williamsburg, Virginia (Appendix F). For the flux model, ^{22}Na flux in is determined as a function of precipitation. ^{22}Na flux was calculated from precipitation samples in the Pogonia Watershed (157 mbq/m^2) but not in the Hubbard Brook and Jones Run watersheds. ^{22}Na flux in these other sites can be extrapolated by comparing annual precipitation amount (cm) and annual ^{22}Na flux from existing studies (Figure 15). With this relationship established, ^{22}Na flux in for each watershed can be calculated by scaling the Williamsburg ^{22}Na flux in to total annual rainfall in each watershed. (Table 4).

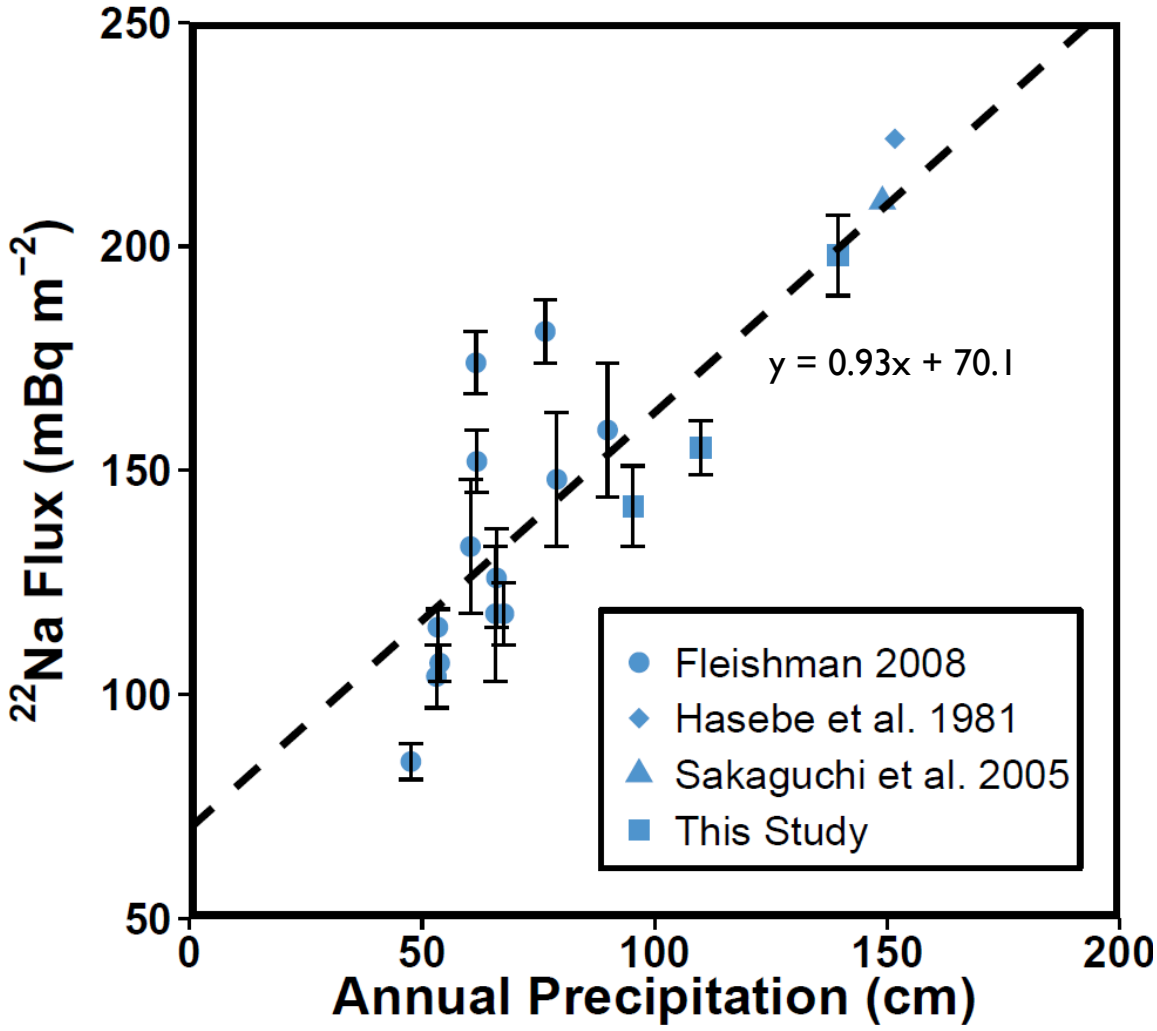

Figure 15. Comparison of annual rainfall values to annual ^{22}Na flux in values. (data from Fleishmann 2008 and Burton 2015).

^{22}Na flux out is determined from the ^{22}Na concentration found in the stream scaled to annual stream discharge. For each site, annual discharge was calculated as a percent of total rainfall for a watershed. From this value, annual ^{22}Na flux out may be calculated (Table 4).

Sample	Annual precipitation (L/m^2)	% ET	^{22}Na stream (mBq/L)	Annual Discharge (L/m^2)	^{22}Na annual flux out (mbq/m^2)
Hubbard Brook (8/29-9/1)	1396	45%	0.162	775	126
Jones Run (9/19-9/25)	1405	55%	0.063	639	40
Pogonia Stream (10/19-10/22), (2/11-2/15)	1319	55%	0.04	600	24

Table 4. Annual ^{22}Na flux out, scaled for each study site as a function of discharge.

Throughfall data was collected to examine the difference in sodium concentration between open rainfall and rain falling through tree leaves. Sodium concentrations were on average 3.28 times greater in throughfall than in rainfall, and sodium flux is on average 2.61 times greater in throughfall than in open rainfall (Figure 9a/b). This discrepancy is due to dry deposition of sodium on tree leaves. The precipitation that follows washes this sodium into the precipitation sample, or in reality, into the water system. Other cations are affected in throughfall as well; concentrations of potassium and calcium were often higher in throughfall as well due to leaching from tree leaves. The current precipitation collection methodology only captures open rainfall and not throughfall. For the ratio model, which takes into account sodium concentrations, throughfall is an important factor that must be accounted for in order to obtain an unbiased age.

^{22}Na Resin Collection Development

The resin bag collection method serves as a great improvement in ease and simplicity of stream water collection. As previously stated, a resin bag containing 80 to 140 grams of resin is placed in the stream for 3 to 4 days minimum, in order to collect sodium equivalent to a minimum of 80 liters of water. The amount of resin needed for successful collection must be adjusted with regard to the original stream chemistry. At future sites, the total dissolved load in the stream must be calculated to know the approximate amount of resin needed for successful equilibration (Figure 16).

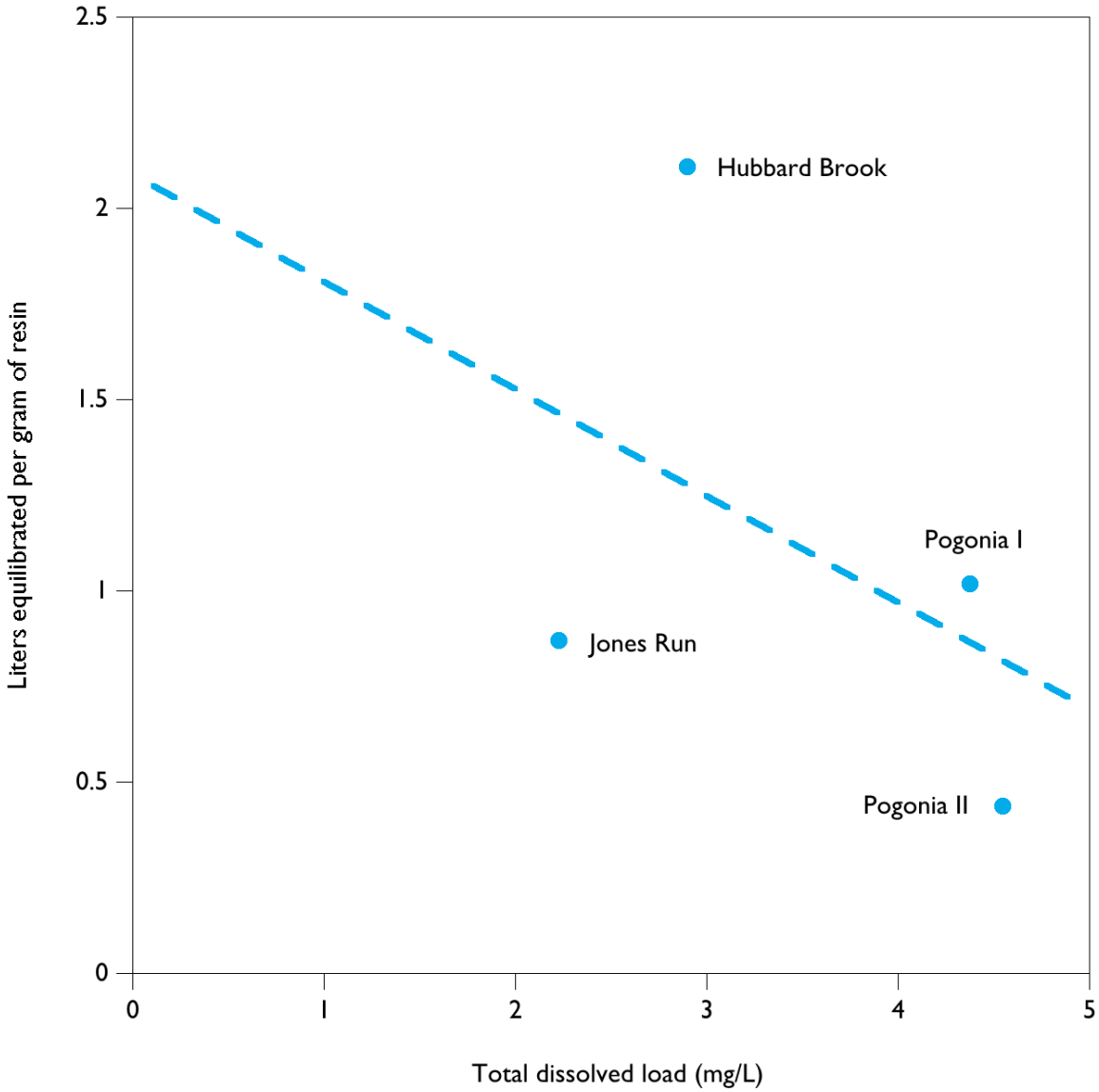

Figure 16. Liters equilibrated per grams of resin with the total dissolved load in each stream.

Another methodological improvement made was resin elution. The efficiency and separation of elution depends on two main factors: (1) the original stream chemistry and (2) the chromatography column conditions. Separation of the sodium and potassium peaks is ideal for removing background noise in detection. Early elution performed on the Hubbard Brook sample (the first elution performed) appeared to have excellent separation of sodium and potassium peaks (Figure 5). The Jones Run sample, with a larger concentration of potassium, revealed the poor separation of the peaks (Figure 11). This poor separation was due to the width of the chromatography column. As the eluting acid dripped onto the resin, the too-wide column only had a small section of the resin interact with the acid (Figure 17a). To counteract this issue, a thinner chromatography column was used. However, due to the large volume of resin used in the pouches (80-100 grams), a long series of attached tubes was necessary to contain the entire resin sample for proper elution. This improved separation of peaks can be seen in the Pogonia II elution (Figure 13; Figure 17b).

Figure 17a. Primary elution method. The inequal distribution of acid for elution can be seen in the wetted center and dry perimeter of the resin.

Figure 17b. Secondary elution method. The Dowex resin was dried and poured into a series of connected tubes for total acid elution.

Evaluating Standard, Ratio, and Flux ^{22}Na Water Age Models

In calculating total age for each watersheds, all three models were tested and compared to an independently derived, non-^{22}Na model (Table 5).

	Independently Derived Age (y)	Error (±)	Decay Model Age (y)	Error (±)	Ratio Model Age (y)	Error (±)	Flux Model Age (y)	Error (±)
Hubbard Brook Watershed (8/29/15-9/1/15)	0.52	0.03	-0.883	0.833	11.57	0.833	1.82	0.56
Jones Run Watershed (9/19/15-9/25/15)	4.4	1.4	2.76	1.02	10.9	1.02	6.24	0.82
Pogonia Stream (10/19/15-10/22/15), (2/11/16-2/15/16)	12.2		4.60	0.385	9.89	0.385	9.39	1.52

Table 5. Age of each watershed calculated from different models.

For Hubbard Brook, an independently derived model was tested by Benettin et al. (2015), who created a model analyzing deuterium (^{2}H) stream content to calculate water transit times. For Pogonia Watershed and Jones Run Watershed, independently derived dating using SF_6 was performed by the USGS Reston Groundwater Dating Laboratory (Burton, 2015; Plummer et al. 2001).

The decay model calculates water age by attributing change in ^{22}Na concentration solely to the decay rate. While this may be a fine method in a completely closed laboratory situation, it makes dangerous assumptions about real world conditions. ^{22}Na concentration can also change due to evapotranspiration. Uptake of water by plants and trees removes water from groundwater systems, but leaves ^{22}Na behind. This decrease in water volume makes any concentration of ^{22}Na (mBq/L) appear larger. Not accounting for this change can lead to a young age bias, as it appears there is a higher concentration of ^{22}Na than there actually is. All three watersheds exhibit this young bias by several years when the decay model is used. This bias is most clearly seen in the Hubbard Brook

sample, where the independently derived age is quite young already (0.52 ± 0.03 years). The decay model actually results in a negative age due to evapotranspiration bias (-0.883 ± 0.833 years). The decay model results in an undesirably young age, and can be considered unfit for any site where evapotranspiration takes place.

The ratio model, comparing the ratio of ^{22}Na and generic Na+, is used with the intention of correcting for evapotranspiration. However, the inclusion of Na+ ions in this equation limits its use. Only streams that do not encounter sodium-containing rocks can be used. If there is sodium present in the sediment or rock underlying the stream, that sodium can enter the stream flow. This unaccounted input in the equation can lead to an old age bias. Pogonia Stream only encounters "clean" Coastal Plain sediments and does not receive sodium inputs from the underlying geology. The Jones Run watershed includes the Harpers, Weverton, and Catoctin formations in the Blue Ridge. The relatively high age given by the ratio model (11.57 ± 0.833 years) as opposed to the independently derived model (4.4 ± 1.4 years) is most likely due to inputs from weathering of the albite schist found in the Harpers formation. Hubbard Brook watershed is also underlain by schist, which when weathered, releases sodium into the streamflow. This also results in an old age bias (10.7 to 12.4 years, as compared to independently derived 0.52 ± 0.03 years).

Another factor contributing to error in the ratio model is dry deposition of sodium on tree leaves, which is then washed into the water system with the next rainfall. Precipitation collection analyzed for sodium concentrations only captured open rainfall and not throughfall. Measurements of throughfall found sodium concentrations were on average 3.28 times greater in throughfall than in open rainfall. In a forested watershed

like the ones sampled in this study, the majority of precipitation contributing to stream flow is throughfall. Age calculation using only open rainfall sodium concentrations in the ratio model thus yields an old age bias. The potentially unpredictable variations in sodium concentration due to geology and throughfall conditions makes the ratio model an unreliable method, yielding an old age bias.

The flux model appears to yield the age most closely correlated with the independently derived age for all watersheds. The flux method corrects for evapotranspiration bias if the stream discharge is calculated as a percent of precipitation, using the percent evapotranspiration model. The flux equation also removes the need to ensure underlying "clean" geology, as Na+ concentrations are not a factor in the final age calculation. The corrective effects of the flux model are most clearly seen in the Hubbard Brook watershed, where the final age range given by the flux model of 1.82 ± 0.56 years best matches the independently derived age of 0.52 ± 0.03 years. The flux model also provides a closely matched age for the Jones Run watershed (6.24 ± 0.82 years as compared to 4.4 ± 1.4 years independently derived). The Pogonia flux model in this study (9.39 ± 1.52 years) does not match the independently derived age (12.2 years). This may be due to the combination of the two Pogonia samples, and improper elution of the first Pogonia sample (Figure 12). Seasonal changes in stream flow were not accounted for in combination of the two samples. In comparison to the setbacks associated with the decay model and the ratio model, the flux model provides the most accurate age of all ^{22}Na models (Figure 18).

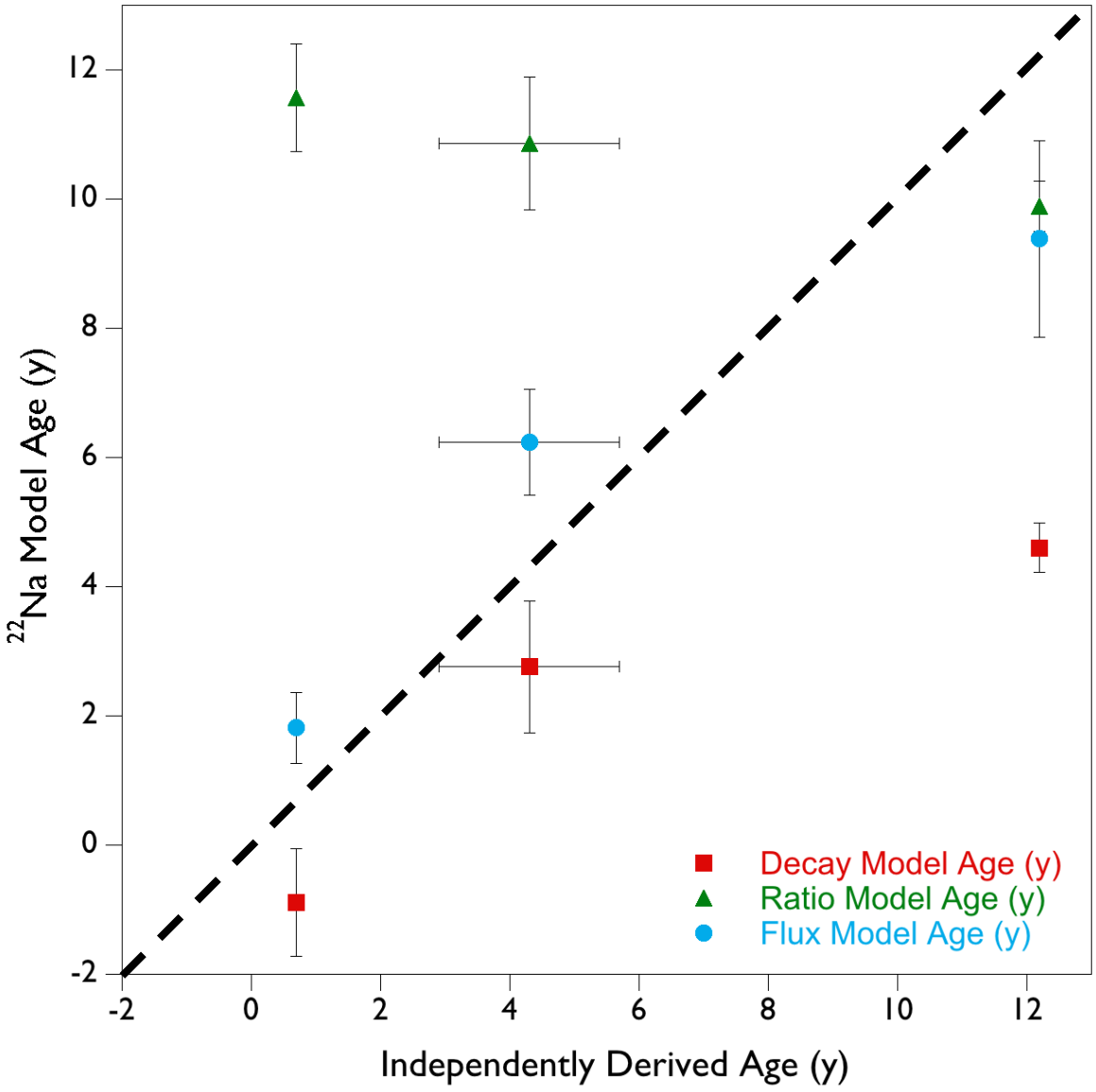

Figure 18. Comparison of each ^{22}Na model to independently derived ages in each watershed.

Conclusion

In this study, the ^{22}Na flux model is shown to be the best method for calculating a "summary" age of water within a single watershed from a single point of discharge, as compared to independently derived ages. Flow points within a single watershed could not be isolated within the Pogonia watershed, but may be a future area of research within a larger watershed. Development of the in-situ resin bag stream water collection method made collection simpler and allowed for expansion of stream water collection to non-local watersheds. ^{22}Na continues to provide a reliable age for the Pogonia watershed, as well as the expanded study sites. The ^{22}Na flux model in particular expands our use of the ^{22}Na model to sodium-containing watersheds while still correcting for evapotranspiration. Future work should include a distinction between throughfall and open rainfall precipitation collection and seasonal changes in streamflow. With changing anthropogenic concentrations of other tracers, ^{22}Na will remain a trustworthy method for dating young fresh waters.

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Appendix A

Detector Testing

Count Setting	Detection Efficiency
NaI	42%
BGO	49%
NaI if BGO	24%
BGO if NaI	24%
BGO if PMT	30%

Preliminary detector efficiency

Sample	^{22}Na Flux (mBq/m^2)
May 2015 Precip	8.55
June 2015 Precip	9.67

Precipitation sample ^{22}Na Flux

Test Sample	Molarity	Percent Sample by Volume	Temperature	Notes
KCl	1	45%	Room temperature	Cloudy solution. Reverted to liquid from gel overnight.
KCl	2	25%	Refrigerated	Cloudy solution. Bubbles formed; added 1 ml cocktail and shook to eliminate.
NaCl	2	25%	Refrigerated	Cloudy solution, liquid did not gel.
KCl	2	25%	Refrigerated	Solution separated overnight and did not gel.
KCl	1	45%	Room temperature	Opaque solution
KCl	1	40%	Room temperature	Opaque solution; cleared after 1 hour.

Percent sample and scintillation cocktail tests

Time (minutes)	40% KCl (%T)	45% KCl (%T)	40% KCl Cold (%T)	40% NaCl Cold (%T)
0	0.4889	0.4527		
30	0.511	0.4113	0.8456	0.25347
60	0.4751	0.3761	0.9149	0.2946
90		0.3912	0.582	0.3085
120		0.7198	0.4871	
150		0.7164	0.435	
180		0.4835	0.4718	
210		0.4366		
Overnight	0.9036	0.8394	0.6686	0.4833

Percent transmissivity (sample clarity) tests

Appendix B

Williamsburg Precipitation: Open v. throughfall sodium concentrations and fluxes

Storm Date	Open [Na] (mg/L)	Throughfall [Na] (mg/L)	Difference Factor	Open Volume (mm)	Open Flux (mg/m^2)	Throughfall Volume (mm)	Throughfall Flux (mg/m^2)	Difference Factor
6/20/2015	0.14	0.42		4.50	0.64	3.50	1.48	
6/24/2015	0.04	0.18		7.50	0.28	6.00	1.09	
6/25/2015	0.04	0.11		7.50	0.27	4.50	0.50	
7/2/2015	0.02	0.10		4.50	0.11	2.50	0.24	
7/4/2015	0.09	0.07		12.0	1.05	11.5	0.84	
7/13/2015	0.03	0.69		3.50	0.09	1.25	0.86	
7/27/2015	0.56	0.50		3.00	1.69	2.00	1.00	
7/31/2015	0.11	0.22		3.50	0.40	1.25	0.27	
8/6/2015	0.03	1.16		6.50	0.17	5.50	6.38	
8/7/2015	0.12	0.42		2.50	0.31	1.00	0.42	
AVERAGE	0.12	0.39	**3.28**		0.50		1.31	**2.61**

Appendix C

Resin Elution: Sodium concentrations, mass, and total equilibrated liters

Hubbard Brook				
Sample	[Na] (mg/L)	Na (mg)	Total Na Collected (mg)	Equilibrated Liters
Hubbard Brook Stream	1.82			
0-50	1049	52.0		
50-100	1530	76.5		
100-150	1485	75.3		
150-200	1070	53.7		
200-250	624	31.2		
250-300	344	18.8	308	169

Jones Run				
Sample	[Na] (mg/L)	Na (mg)	Total Na Collected (mg)	Equilibrated Liters
Jones Run Stream	0.795			
0-50 ml eluted	229	11.0		
50-100	355	17.8		
100-150	371	19.2		
150-200	364	19.7		
200-250	327	16.2		
250-300	255	12.7	96.8	122

Pogonia I				
Sample	[Na] (mg/L)	Na (mg)	Total Na Collected (mg)	Equilibrated Liters
Pogonia Stream	2.37			
0-50	846	42.2		
50-100	158	7.97		
100-150	34.2	1.69		
150-200	93.1	4.59		
200-250	368	18.1		
250-300	189	9.64		
300-350	380	19.0		
350-400	230	11.6		
400-450	66.6	3.35		
450-500	24.9	1.23		
500-550	28.0	1.40	121	51

Pogonia II				
Sample	[Na] (mg/L)	Na (mg)	Total Na Collected (mg)	Equilibrated Liters
Pogonia Stream	2.54			
0-50	391	19.5		
50-100	299	14.8		
100-150	307	15.4		
150-200	304	15.3		
200-250	243	12.5		
250-300	154	7.75		
300-350	47.0	2.40		
350-400	13.4	0.67		
400-450	7.53	0.38		
450-500	6.36	0.32	89.0	35

Appendix D

Age Calculation: Decay Model

Hubbard Brook			
[^{22}Na+] Stream (mBq/L)	[^{22}Na+] Precip (mBq/L)	Decay rate	Age (y)
0.172	0.11	0.26	-1.72
0.152	0.15	0.26	-0.05

Jones Run			
[^{22}Na+] Stream (mBq/L)	[^{22}Na+] Precip (mBq/L)	Decay rate	Age (years)
0.07	0.11	0.26	1.74
0.056	0.15	0.26	3.78

Pogonia Stream			
[^{22}Na+] Stream (mBq/L)	[^{22}Na+] Precip (mBq/L)	Decay rate	Age (years)
0.05	0.11	0.26	4.22
0.03	0.15	0.26	4.99

Appendix E

Age Calculation: Ratio Model

Hubbard Brook					
[Na+] Stream (mg/L)	[^{22}Na+] Stream (mBq/L)	[Na+] Precip (mg/L)	[^{22}Na+] Precip (mBq/L)	Decay rate	Age (years)
1.85	0.172	0.0724	0.11	0.26	10.7
1.85	0.152	0.0724	0.15	0.26	12.4

Jones Run					
[Na+] Stream (mg/L)	[^{22}Na+] Stream (mBq/L)	[Na+] Precip (mg/L)	[^{22}Na+] Precip (mBq/L)	Decay rate	Age (years)
0.795	0.07	0.0970	0.11	0.26	9.8
0.795	0.056	0.0970	0.15	0.26	11.9

Pogonia Stream					
[Na+] Stream (mg/L)	[^{22}Na+] Stream (mBq/L)	[Na+] Precip (mg/L)	[^{22}Na+] Precip (mBq/L)	Decay rate	Age (years)
2.455	0.05	0.619	0.11	0.26	9.50
2.455	0.03	0.619	0.15	0.26	10.3

Appendix F

Age Calculation: Flux Model

Hubbard Brook			
^{22}Na annual flux out (mbq/m^2)	^{22}Na annual flux in (mbq/m^2)	Decay rate	Age (years)
144	199.94	0.26	1.26
108	199.94	0.26	2.37

Jones Run			
^{22}Na annual flux out (mbq/m^2)	^{22}Na annual flux in (mbq/m^2)	Decay rate	Age (years)
49.2	200.74	0.26	5.42
32	200.74	0.26	7.05

Pogonia Stream			
^{22}Na annual flux out (mbq/m^2)	^{22}Na annual flux in (mbq/m^2)	Decay rate	Age (years)
22	171.1	0.26	7.87
10	171.1	0.26	10.90

Williamsburg, Virginia: Flux Data										
	Collection Window	^{22}Na (mBq/L)	Error ^{22}Na (mBq/L)	Precip (cm)	Precip (L/m^2)	Annual Precip (L/m^2)	^{22}Na flux (mBq/m^2)	Error ^{22}Na flux (mBq/m^2)	Annual ^{22}Na flux in (mBq/m^2)	Error Annual ^{22}Na flux in (mBq/m^2)
2012	02/01-02/29	0.18	0.021	7.87	78.7		14.2	1.6		
	03/01-04/25	0.15	0.012	11.42	114.2		17.1	1.4		
	04/26-05/30	0.183	0.019	6.99	69.9		12.4	1.3		
	05/31	0.174	0.028	2.04	20.4		3.5	0.6		
	06/01	0.101	0.018	3.81	38.1		2.6	0.5		
	06/02-07/08	0.18	0.018	8.38	83.8		15.1	1.5		
	07/09/12	0.104	0.035	5.69	56.9		5.2	1.7		
	07/22/12	0.045	0.009	11.48	114.8		5.1	1		
	7/28-9/1	0.161	0.012	21.24	212.4		34.2	2.6		
	9/2-9/28	0.055	0.014	9.54	95.4		5.2	1.3		
	9/29-12/26	0.107	0.013	23.11	231.1		24.8	3		
	1/14-1/18	0.07	0.012	10.55	105.5		7.4	1.2		
	02/08/13	0.021	0.014	4.19	41.9	1263.1	0.8	0.5	147.6	18.2
2013	1/31 - 2/26	0.097	0.016	6.12	61.2		5.9	1		
	3/5-3/12	0.176	0.017	4.14	41.4		7.3	0.7		
	3/24-4/12	0.189	0.017	8.37	83.7		15.8	1.4		
	4/19/2013	0.157	0.022	2.06	20.6		3.2	0.4		
	4/29/2013	0.248	0.024	4.75	47.5		11.8	1.1		
	5/7-5/9	0.337	0.04	2.8	28		9.4	1.1		
	5/23/2013	0.218	0.045	13.52	135.2		29.5	6.1		
	6/3/2013	0.111	0.016	4.06	40.6		4.5	0.7		
	6/7/2013	0.013	0.009	5.88	58.8		0.8	0.5		
	6/8-6/9	0.014	0.008	6	60		0.8	0.5		
	6/10-6/27	0.054	0.015	9.04	90.4		4.9	1.4		
	6/28-7/10	0.073	0.011	8.18	81.8		6	0.9		
	7/11-7/23	0.082	0.011	7.19	71.9		5.9	0.8		
	7/24-8/2	0.156	0.017	4.79	47.9		7.5	0.8		
	8/3-8/6	0.277	0.03	3.36	33.6		9.3	1		
	8/7-8/31	0.128	0.012	7.03	70.3		9	0.9		
	9/1-9/30	0.12	0.016	2.72	27.2		3.2	0.4		
	10/1-10/16	0.08	0.017	7.79	77.9		6.3	1.3		
	10/17-11/25	0.091	0.017	1.89	18.9		0.8	0.2		
	11/26-12/9	0.101	0.018	10.07	100.7		10.2	1.9		
	12/10-12/17	0.188	0.02	4.86	48.6		9.2	1		
	12/18-1/13	0.047	0.017	12.82	128.2	1374.4	6	2.2	167.3	26.3